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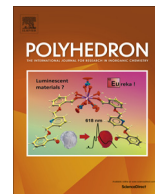
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New crystal packing arrangements in radical cation salts of BEDT-TTF with $[\text{Cr}(\text{NCS})_6]^{3-}$ and $[\text{Cr}(\text{NCS})_5(\text{NH}_3)]^{2-}$



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ABSTRACT

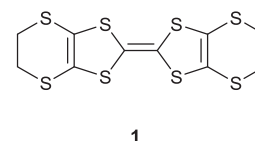
BEDT-TTF forms three packing arrangement styles in its radical cation salts with $[\text{Cr}(\text{NCS})_6]^{3-}$ in two of which two *trans*-oriented isothiocyanate ligands penetrate the BEDT-TTF layers either at the point where a solvent (nitrobenzene) is incorporated in a stack of donors or by four donor molecules forming a “tube” motif to accept a ligand at each end along with a small solvent molecule in between (acetonitrile). The $[\text{Cr}(\text{NCS})_5(\text{NH}_3)]^{2-}$ ion forms a related crystal packing arrangement with BEDT-TTF with a reduction in the number of “tube” motifs needed to accept an isothiocyanate ligand.

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1. Introduction

Radical cation salts provide the opportunity to combine together in the same crystal lattice multiple physical properties which may not usually be found together. The organic donor molecule BEDT-TTF **1** has provided a large number of such salts, usually in the form of segregated stacks of donor and anion molecules. Typically a simple anion such as Cl^- , linear I_3^- , tetrahedral BF_4^- , or octahedral PF_6^- produce an array of packing arrangements of the donor molecules which leads to a variety of conducting properties such as metals, semiconductors, and superconductors [1–4]. The inclusion of a layer of anions introduces the possibility of multifunctionality. One of the main areas of focus has been the use of magnetic anions to introduce localised magnetic moments into these materials. Halogenometallate anions of the type MX_4 ($\text{M} = \text{Fe}, \text{Mn}, \text{Co}, \text{Zn}$; $\text{X} = \text{Cl}, \text{Br}$) [5–7] and MCl_6 ($\text{M} = \text{Re}$ and Ir) [8] have produced a number of paramagnetic semiconducting salts with BEDT-TTF while a number of salts have been obtained from octahedral anions of type $\text{M}(\text{CN})_6$ ($\text{M} = \text{Fe}, \text{Co}, \text{Cr}$) [9]. The most extensive family of BEDT-TTF salts containing magnetic anions are those containing *tris*(oxalato)metallate, $(\text{BEDT-TTF})_x[(\text{A})\text{M}^{3+}(\text{C}_2\text{O}_4)_3]\cdot\text{Guest}$ ($\text{A} = \text{K}^+, \text{H}_3\text{O}^+, \text{Li}^+, \text{Na}^+, \text{NH}_4^+$; $\text{M}^{3+} = \text{Fe}, \text{Cr}, \text{Ga}, \text{Al}, \text{Co}, \text{Ru}, \text{Cu}, \text{Ge}$) in which the *tris*(oxalato)metallate anions along with the counter cation (A) produce a

honeycomb arrangement in the anion layer which is capable of including a guest molecule within the honeycomb [10–14].



The influence of chirality on the electromagnetic properties of radical cation salts is also very topical [15–18], and electrocrystallisation of BEDT-TTF with the racemic $[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ trianion from a chiral electrolyte has produced a family of semiconducting salts of the formula $(\text{BEDT-TTF})_3\text{AM}(\text{C}_2\text{O}_4)_3\cdot\text{Guest}$ ($\text{A} = \text{Na}, \text{NH}_4$; $\text{M} = \text{Cr}, \text{Al}$) containing a single enantiomer of $[\text{M}(\text{C}_2\text{O}_4)_3]^{3-}$ [19–22]. Although other chiral anions have been used with BEDT-TTF, e.g., $[\text{Fe}(\text{croconate})_3]^{3-}$, $[\text{Cr}(2,2'\text{-bipy})(\text{oxalate})_2]^-$ and TRISPHAT^- , most are racemic and only the salt with $[\text{Sb}_2(\text{l-tartrate})_2]^{2-}$ has an enantiopure anion [23–25], and none has produced a family as extensive as that from *tris*(oxalato)metallate.

Here we report some new salts of BEDT-TTF with $[\text{Cr}(\text{NCS})_6]^{3-}$ and $[\text{Cr}(\text{NCS})_5(\text{NH}_3)]^{2-}$ obtained serendipitously in work aimed at combining BEDT-TTF with chiral metal complexes of chromium. A few salts of BEDT-TTF with anions containing isothiocyanate are known: the salt $\alpha\text{-(BEDT-TTF)}_2\text{Cs}[\text{Co}(\text{NCS})_4]$ shows metallic behaviour down to a metal–insulator transition at 20 K, though

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this salt has no close BEDT-TTF sulfur...SCN contacts [26] and $(\text{BEDT-TTF})_2\text{Cu}(\text{NCS})_2$ [27,28], in which the Cu^+ and SCN^- ions form a layer structure, shows superconductivity below *ca.* 10 K. Our results will be set in the context of several known phases containing BEDT-TTF and $[\text{Cr}(\text{NCS})_6]^{3-}$ [29–31], and the reinterpretation of a phase containing $[\text{Cr}(\text{NCS})_5\text{NH}_3]^{2-}$ which had been communicated [32] to the Cambridge Structural Database [33].

2. Discussion

During work directed at preparing radical cation salts of BEDT-TTF with chiral anions of type $\text{Cr}(\text{NCS})_4\text{L}$ where **L** was a single enantiomer of (+)-BINOL or 4*S*-4-isopropyl-2-(2'-pyridyl)-1,3-oxazoline, electrocrystallisation of BEDT-TTF with the ammonium salts of these two chiral anions in nitrobenzene/acetonitrile led to growth of two quite different phases, **A** and **B** respectively. These contain BEDT-TTF with $[\text{Cr}(\text{NCS})_6]^{3-}$ with either nitrobenzene or acetonitrile, but no chiral components. Two examples of a third phase, **C**, have been reported briefly in the literature [30,31]. We also report a salt containing the $[\text{Cr}(\text{NCS})_5(\text{NH}_3)]^{2-}$ dianion, which was produced by a similar experiment to that which produced phase **B** but using chlorobenzene/ethanol rather than acetonitrile/nitrobenzene as solvent.

To pack layers of octahedral anions containing six projecting ligands with layers of BEDT-TTF donors requires that two of the ligands must penetrate the donor layers. The packing arrangements of the BEDT-TTF units for phases **A** and **B** are shown in Fig. 1. Thus, **A** has the composition $(\text{BEDT-TTF})_4[\text{Cr}(\text{NCS})_6]\cdot\text{PhNO}_2$ in which the nitrobenzene and BEDT-TTF units are stacked together, and layers composed of these stacks are separated by layers of $[\text{Cr}(\text{NCS})_6]^{3-}$ anions, two of whose *trans* oriented NCS groups

penetrate into the adjacent BEDT-TTF/nitrobenzene layers towards nitrobenzene molecules. The corresponding solvate with benzonitrile rather than nitrobenzene has been reported [29]. Phase **B**, $(\text{BEDT-TTF})_4[\text{Cr}(\text{NCS})_6](\text{CH}_3\text{CN})$, is totally different, and does not involve stack formation but involves four BEDT-TTF units forming the sides of a long rectangular “tube” motif, and these “tubes” are then packed against each other to form layers. These layers are separated by layers of $[\text{Cr}(\text{NCS})_6]^{3-}$ anions, and a pair of *trans*-oriented NCS ligands are inserted into “tube” units to either side. Thus, each “tube” unit has a NCS ligand inserted at each end and an acetonitrile molecule is trapped in the centre of the “tube”. A further phase, phase **C**, has been reported in the literature with formula $(\text{BEDT-TTF})_5[\text{Cr}(\text{NCS})_6]\text{X}$ where layers of stacked BEDT-TTF units are separated by layers composed of $[\text{Cr}(\text{NCS})_6]^{3-}$ anions and X, where X is either neutral BEDT-TTF molecules ($\text{X} = 0.5(\text{BEDT-TTF})$) [30,31] or tetrabutylammonium cations and THF molecules ($\text{X} = (\text{N}(\text{C}_4\text{H}_9)_4)^+\cdot\text{THF}$) [31]. In these cases, the additional components in the anion layers increase the thickness of these layers, so that there is no need for BEDT-TTF stacks to be penetrated by the NCS ligands. No coordinates were reported for either of the two examples of phase **C**.

Finally, we report a salt containing the related dianion $[\text{Cr}(\text{NCS})_5(\text{NH}_3)]^{2-}$ which contains layers composed of “tube” units (as described for phase **B**), with a pair of donors and a single donor all packed together. The “tube” unit contains solvent, and the layers are separated by layers of $[\text{Cr}(\text{NCS})_5(\text{NH}_3)]^{2-}$ anions and solvent. In our example the solvent is ethanol, and a very similar phase [32], briefly communicated in the Cambridge Structural Database [33], is reinterpreted here as the corresponding phase with dichloromethane as the solvent. Only the NCS ligand *trans* to the ammonium ligand penetrates the “tube”, hence the need for fewer “tube” motifs in the packing arrangement than in phase **B**.

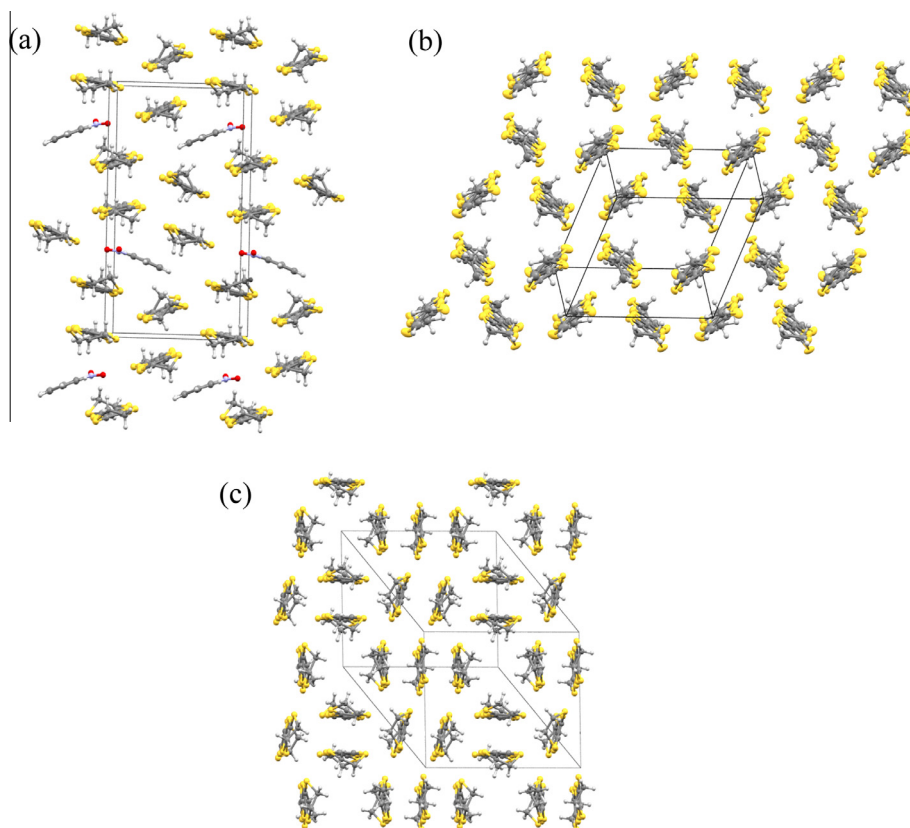


Fig. 1. Crystal packing arrangements of BEDT-TTF units in (a) phase **A** and (b) phase **B** containing the $[\text{Cr}(\text{NCS})_6]^{3-}$ trianion and (c) the phase formed with the $[\text{Cr}(\text{NCS})_5\text{NH}_3]^{2-}$ dianion. Solvents included in the “tube” units in (b) and (c) have been omitted for clarity.

2.1. (BEDT-TTF)₄[Cr(NCS)₆].PhNO₂, phase A

X-ray diffraction data for the nitrobenzene solvate, phase A, were collected using synchrotron radiation ($\lambda = 0.6942 \text{ \AA}$) at 120 K. Crystals are monoclinic and in space group $P2_1$ with four BEDT-TTF donor molecules, one $\text{Cr}(\text{NCS})_6$ anion and a nitrobenzene molecule in the asymmetric unit. The crystal packing arrangement is shown in Figs. 1(a), 2 and 3. The four crystallographically independent donor molecules are aligned with their main axes roughly parallel and organised in two pairs which pack along with the nitrobenzene molecules in the *ab* plane (Fig. 1(a)). Adjacent planes are separated by planes of $[\text{Cr}(\text{NCS})_6]^{3-}$ counterions which insert an isothiocyanate group into the spaces near the nitrobenzene molecules in the two neighbouring planes (Fig. 2). The relative arrangement of the planes of $[\text{Cr}(\text{NCS})_6]^{3-}$ anions and planes of BEDT-TTF and nitrobenzene molecules is shown in Fig. 3.

The four donors lie in two pairs (Fig. 1). One pair of donors lies with the planes defined by their sulfur atoms nearly parallel (at 2.4°) and approximately face-to-face with four short $\text{S}\cdots\text{S}$ contacts between their TTF sulfur atoms in the range $3.4405(16)$ – $3.6112(17) \text{ \AA}$. This pair is sandwiched between nitro groups of two solvent molecules. Calculations of the charges on these donors from their molecular geometry following the procedure of Guionneau et al. [34] gives values of +1.01 and +1.00, suggesting they are a pair of monocations. The second pair of donors lies to one side of the first pair and more distant from the solvent's nitro groups. The donors are almost parallel (at 0.61°) but there is a significant sideways offset between the donors such that there are only two short $\text{S}\cdots\text{S}$ contacts between the TTF sulfur atoms of $3.6136(16)$ and $3.6390(16) \text{ \AA}$. The calculated charges on these donors are +1.13 and +0.24, i.e., one donor carries much less charge than the other three. The sum of charges over the four donors is +3.38, which, bearing in mind an error of ca. 0.1 in each calculation, is similar to the anticipated total charge of +3. Confirmation of the charge distribution was sought from Raman spectroscopic measurements, which identified two peaks in the region in which the active symmetric stretch for the central $\text{C}=\text{C}$ occur. One broad peak was exhibited at $\nu = 1430\text{--}1465 \text{ cm}^{-1}$ and a minor peak at $\nu = 1493\text{--}1497 \text{ cm}^{-1}$, indicating the presence of BEDT-TTF molecules in oxidation states +0.6–1.0 and +0.1–0.2 according to the

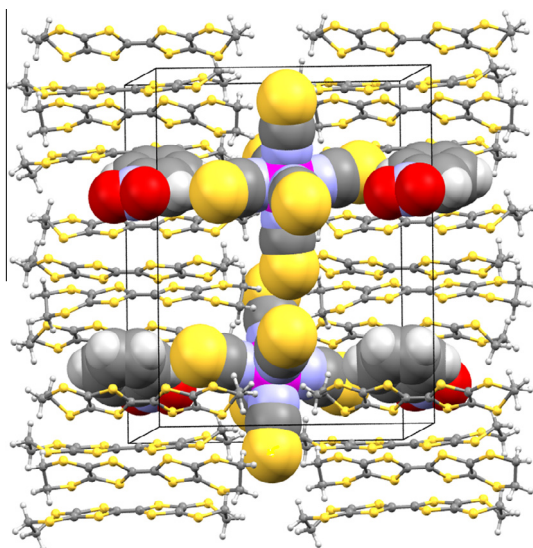


Fig. 2. View of the crystal packing of $(\text{BEDT-TTF})_4[\text{Cr}(\text{NCS})_6]\cdot\text{C}_6\text{H}_5\text{NO}_2$ viewed along the *a* axis with the *b* axis vertical, showing how the anions direct two isothiocyanate ligands towards the nitrobenzene molecules lying within the donor stacks.

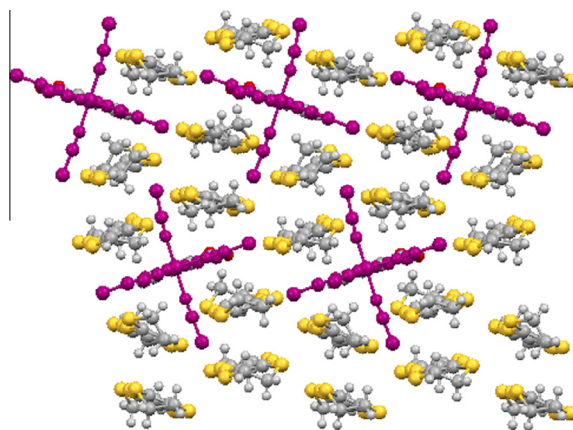


Fig. 3. View of the crystal packing of $(\text{BEDT-TTF})_4[\text{Cr}(\text{NCS})_6]\cdot\text{C}_6\text{H}_5\text{NO}_2$ viewed approximately along the *c* axis with the *b* axis vertical, showing the layer of $[\text{Cr}(\text{NCS})_6]^{3-}$ anions lying over the BEDT-TTF/nitrobenzene layer. The nitrobenzene molecules lie directly behind the $[\text{Cr}(\text{NCS})_6]$ anions.

method of Wang et al. [35] which are consistent with the oxidation states for the donor molecules calculated from the X-ray crystal structure.

Despite the presence of the nitrobenzene molecules in the donor layers there is an extensive network of more than twenty short $\text{S}\cdots\text{S}$ contacts $<3.6 \text{ \AA}$ between the pairs of donor molecules, with nine in the range $3.3086(17)$ – $3.3993(17) \text{ \AA}$ providing potential conduction pathways in the *ab* plane. The pair of *trans*-oriented isothiocyanate ligands which are directed towards nitrobenzene molecules are displaced from the normal reasonably linear geometry at nitrogen by angles of 27.1° and 17.3° . The isothiocyanate sulfur atoms make $\text{S}\cdots\text{S}$ contacts with donor molecules; the four ligands which do not penetrate the donor stacks each make one (or, in one case, two) $\text{S}\cdots\text{S}$ contacts in the range $3.4870(17)$ – $3.5961(16) \text{ \AA}$, while the other two ligands make longer $\text{S}\cdots\text{S}$ contacts in the range $3.6652(19)$ – $3.7657(17) \text{ \AA}$. Conductivity measurements in the range 96–298 K showed the crystal to be a semiconductor with a room temperature conductivity of $6.4 \times 10^{-3} \text{ S cm}^{-1}$ falling to 2.6×10^{-5} at 100 K. The activation energy is estimated as 0.11 eV in the range 150–298 K, but at lower temperatures falls to 0.04 eV. The structure is isomorphous with the $(\text{BEDT-TTF})_4\text{Cr}(\text{NCS})_6\cdot\text{C}_6\text{H}_5\text{CN}$ structure reported by Th  tiot et al. [29] with just a change of included solvent. The same pattern of charge distribution between the donor molecules is also observed in this structure which shows a slightly higher room temperature conductivity of $1.4 \times 10^{-2} \text{ S cm}^{-1}$ with activation energy 0.24 eV.

2.2. (BEDT-TTF)₄[Cr(NCS)₆](CH₃CN), phase B

The crystals of this acetonitrile solvate were triclinic in space group $P\bar{1}$. The unit cell comprises four BEDT-TTF donors, a $\text{Cr}(\text{NCS})_6^{3-}$ anion and a molecule of acetonitrile, with two donors crystallographically unique and the anion and solvent lying on crystallographic centres of symmetry. Four parallel donor molecules form the walls of a long “tube” oriented along the *c* axis of the unit cell (Figs. 1(a) and 4). The angles between the planes of the donors, defined by their eight sulfur atoms, are 69° and 111° . $\text{Cr}(\text{NCS})_6^{3-}$ anions lie at each end of the “tube” and one isothiocyanate ligand from each of these anions is inserted into each end of the “tube” (Figs. 4 and 5). An acetonitrile molecule is trapped between the two terminal ligand sulfur atoms at the centre of the “tube”, and is disordered across a centre of symmetry. The $\text{S}\cdots\text{S}$ contacts between the donor molecules forming the “walls” of the tube lie in the range $3.523(4)$ – $4.147(4) \text{ \AA}$, with the

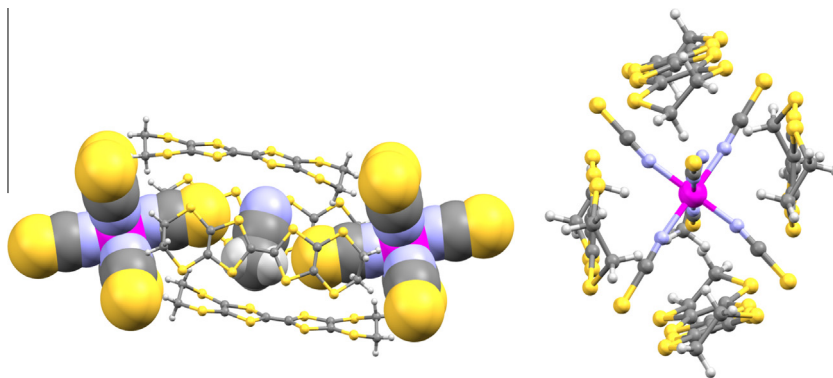


Fig. 4. The “tube”-like packing motif in $(\text{BEDT-TTF})_4[\text{Cr}(\text{NCS})_6](\text{CH}_3\text{CN})$, formed by four BEDT-TTF units capped by two $\text{Cr}(\text{NCS})_6^{3-}$ anions viewed perpendicular to “tube” axis (left) and along “tube” axis (right).

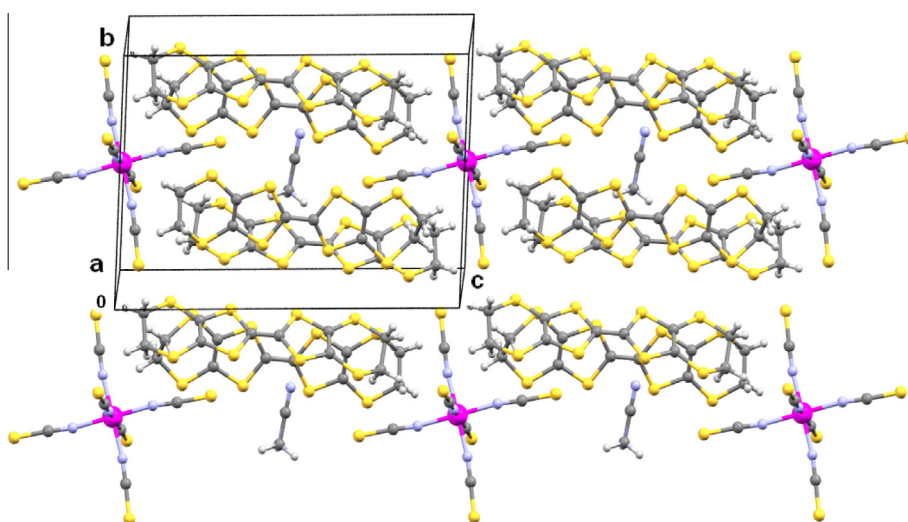


Fig. 5. Crystal packing arrangement for $(\text{BEDT-TTF})_4[\text{Cr}(\text{NCS})_6](\text{CH}_3\text{CN})$.

shortest contacts involving at least one dithiin sulfur atom. “Tube” motifs lie side by side to complete the donor packing in the *ab* plane. Two donors from the “walls” of the “tube” each make face-to-face contacts with a donor of a neighbouring “tube” with $\text{S} \cdots \text{S}$ contacts of 3.765(3) and 3.769(3) Å between dithiol S atoms. The other two donors from the “tube walls” each make side-to-side contacts with two other donors with $\text{S} \cdots \text{S}$ contacts between dithiin sulfurs of 3.372(4) and 3.566(3) Å, and are oriented edge-to-face with two further donor molecules with $\text{S} \cdots \text{S}$ separations between dithiin sulfurs of 3.443(4) and 3.632(5) Å to one donor and 4.161(5) and 4.199(5) Å to the other. The $\text{Cr}(\text{NCS})_6^{3-}$ units lie in the *ab* plane to either side of the donor plane, and the angles at nitrogen on the complex anion lie in the range 168–172°. The charges on the two crystallographically independent donors are estimated from their molecular geometries to be +0.6 and +0.8, so that for four donors the total charge is *ca.* +2.8, which counterbalances the -3 charge of the anion. Stretches in the Raman spectrum at 1416 and 1460 cm^{-1} indicate charge states of +0.8 to +1.0 and +0.6 to +0.7, respectively, consistent with the results based on molecular geometry. No resistivity measurements could be made due the small size and fragile nature of the crystals. This type of packing also occurs in two related materials: $(\text{BEDT-TTF})_4[\text{Fe}(\text{NCS})_6] \cdot \text{CH}_2\text{Cl}_2$ [36] and $(\text{BEDT-TTF})_4[\text{Cr}(\text{NCSe})_6] \cdot \text{CH}_2\text{Cl}_2$ [37], in both of which a disordered dichloromethane molecule is located at the centre of the “tube”.

2.3. $(\text{BEDT-TTF})_7[\text{Cr}(\text{NCS})_5(\text{NH}_3)]_2(\text{solvent})$

This phase, in space group $P\bar{1}$, and with the modified anion where one isothiocyanate is replaced by ammonia shows yet another packing mode for the BEDT-TTF donors. The donors and anions pack in parallel layers perpendicular to the *c* axis with solvent included in both. The packing of the donors contains the “tube” motif which is provided by two pairs of centrosymmetrically related donor molecules, along with a face-to-face centrosymmetric dimer of donors and a single donor which lies across another centre of symmetry, and is shown in Figs. 1(c) and 6. “Tube” units are packed in lines in one direction, but separated in the second direction by the centrosymmetric donor, with the extra donor pair lying to either side of the latter donor. Ethanol lies in the “tube” and is disordered across a centre of symmetry at the middle of the tube, and a complex anion at each end of the tube inserts an isothiocyanate ligand into the “tube”. The ammonia ligand lies *trans* to this isothiocyanate and adjacent to the ends of the face-to-face donor pair in the next donor layer. In the complex anion layer there are cavities located near the ammonia ligands which are occupied by disordered solvent, ethanol and water. The nearest contacts to the ammonia hydrogen atom are a $\text{S} \cdots \text{H}$ contact (2.65 Å) to a neighbouring $[\text{Cr}(\text{NCS})_5\text{NH}_3]^{2-}$ ion, and a hydrogen bond to a partially occupied water. The crystals were too fragile for conductivity measurements

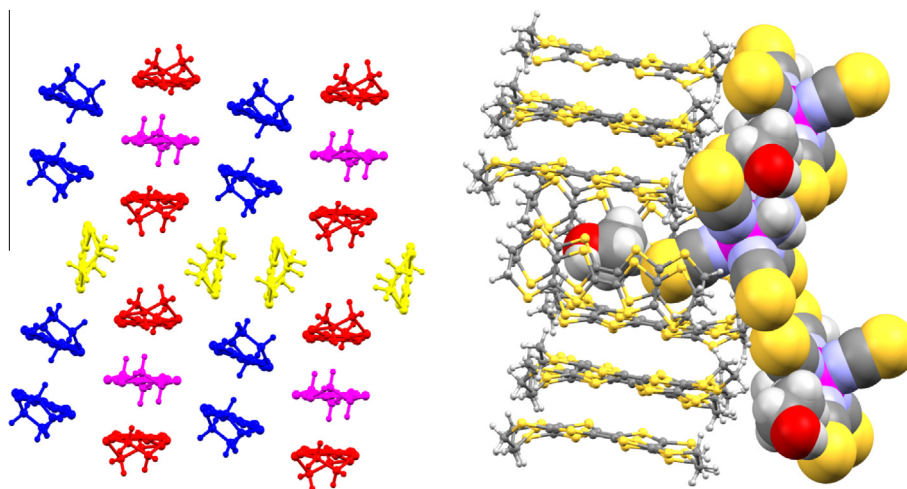


Fig. 6. Left: packing arrangement of BEDT-TTF molecules in $(\text{BEDT-TTF})_7[\text{Cr}(\text{NCS})_5\text{NH}_3]_2$, solvent, showing the “tube” motif (yellow and red donors), a pair of donors (blue) and a single one lying on a centre of symmetry (pink), viewed down the c axis with the b axis vertical. The solvent in the “tubes” is omitted for clarity. Right: packing arrangement showing how the complex anion layer directs a ligand alternately into opposite layers, and the positions of the ethanol molecules within the BEDT-TTF layer and among the complex anions, viewed down the a axis with the b axis vertical (right). (Colour online.)

to be made. A further structure [32] communicated to the Cambridge Structural Database, has been re-examined and found to be the dichloromethane solvate analogue of this structure, containing ordered dichloromethane in the solvent layer, and a further dichloromethane molecule at the centre of the tube, and disordered across a centre of symmetry. These are the first two examples of compounds containing this anion. The assignment of the sixth ligand as ammonia in both structures is supported by the Cr–NH₃ bond lengths (2.056(5) and 2.057(9) Å) which are very similar to that observed in $(\text{BEDT-TTF})_2[\text{Cr}(\text{NCS})_4(\text{NH}_3)_2]$ (2.07 Å) [38] and other cases [39].

3. Conclusion

The need to accommodate an octahedral ion with side arms three atoms long in salts of BEDT-TTF with $[\text{Cr}(\text{NCS})_6]^{3-}$ can be solved in several ways. Either two ligand side arms are inserted into BEDT-TTF/aromatic solvent stacks at the points where the smaller solvent molecules occur, or four BEDT-TTF molecules form a channel to incorporate the side arms at either end, with the central space filled by solvent. Alternatively, the anion layer is bulked out with other molecules so that there are no protruding side arms to be accommodated. The novel $[\text{Cr}(\text{NCS})_5\text{NH}_3]^-$ anion can be accommodated by the donor layers which have adapted to contain enough channels formed by four BEDT-TTF molecules to receive the isothiocyanate ligand trans to the ammonia ligand. Chromium(III) complexes are regarded to be kinetically very slow to undergo substitution reactions, nevertheless this type of behaviour has been observed before under electrocrystallisation conditions where the cells are left for a week or more [40]. It is also notable that enantiopure Cr(III)tris(oxalate) racemises during electrocrystallisation [41]. Furthermore, the nature of electrocrystallisation is that most stable arrangement of donor cations with one of the anionic species are present in solution will be formed, and the anions with the smaller ligands have been incorporated more easily into the crystal structures.

4. Experimental

4.1. $\text{NH}_4[[(+)\text{BINOL}]\text{Cr}(\text{NCS})_4]_2$

Reinecke's salt (1.0 g, 2.97 mmol) and (*R*)-(+)-2,2-bi(naphthol) (0.85 g, 2.97 mmol) in acetonitrile (40 mL) were heated to reflux

under a nitrogen atmosphere for 12 h. Over the course of the reaction, a colour change from pink to purple was observed. The reaction mixture was cooled to room temperature, and evaporated under reduced pressure to around 5 mL. Standing in the fridge overnight afforded a precipitate, which was isolated by filtration and dried *in vacuo* at room temperature to afford **2** (1.80 g, 97%) as a purple solid, m.p. 188 °C (Found: C, 48.7; H, 3.5; N, 12.0. $[\text{Cr}(\text{NCS})_4(\text{C}_{20}\text{H}_{14}\text{O}_2)][\text{NH}_4]$ requires: C, 49.0; H, 3.1; N, 11.9%); ν_{max} (ATR)/ cm^{-1} 3509, 3432, 3153, 2077, 1617, 1595, 1511, 1383, 1318, 1272, 1257, 1219, 1181, 1148, 1024, 823, 814, 748, 564.

4.2. (*S*)-4-Isopropyl-2-(2'-pyridyl)-1,3-oxazoline [42]

L-Valinol (0.7 g, 6.78 mmol), 2-cyanopyridine (0.71 g, 6.78 mmol) and a few crystals of 4-toluenesulfonic acid were heated together in a conventional 800 W microwave oven for 2 min. The crude material was allowed to cool, and purified by chromatography over silica eluting with ethyl acetate/methanol (15:1), affording the pyridyl oxazoline derivative (0.26 g, 20%) as a colourless oil; δ_{H} (400 MHz, CDCl_3) 8.71 (1H, ddd, $J = 4.9, 1.9, 0.8$ Hz, 6-*H*), 8.07 (1H, d, $J = 7.9$ Hz, 3-*H*), 7.78 (1H, dt, $J = 7.8, 1.8$ Hz, 4-*H*), 7.39 (1H, ddd, $J = 7.8, 4.9, 1.1$ Hz, 5-*H*), 4.52 (1H, m, 4'-*H*), 4.22 (1H, dd, $J = 8.2, 7.8$ Hz, 5'-*H*_α), 4.17 (1H, m, 5'-*H*_β), 1.90 (1H, m, CHMe₂), 1.06 (3H, d, $J = 6.9$ Hz, CH₃), 0.95 (3H, d, $J = 6.9$ Hz, CH₃); δ_{C} (100 MHz, CDCl_3) 162.5 (2-*C*), 149.7 (6'-*C*), 146.9 (2'-*C*), 136.6 (4'-*C*), 125.4 (3'-*C*), 123.9 (5'-*C*), 72.9 (4-*C*), 70.7 (5-*C*), 32.7 (CHMe₂), 19.0 (CH₃), 18.4 (CH₃).

4.3. Ammonium [chromium ((*S*)-4-isopropyl-2-(2'-pyridyl)-1,3-oxazoline)tetra-thiocyanate], **3**

(*S*)-4-Isopropyl-2-(2'-pyridyl)-1,3-oxazoline (1.0 g, 5.3 mmol) and Reinecke's salt (1.77 g, 5.3 mmol) were heated to reflux in acetonitrile (60 mL) under an atmosphere of nitrogen overnight. The reaction was allowed to cool to room temperature, and the solvent evaporated. Drying under high vacuum at room temperature afforded **3** (2.58 g, 99%) as a purple gum (Found C, 36.5; H, 3.7; N, 19.9. $\text{C}_{15}\text{H}_{18}\text{CrN}_7\text{OS}_4$ requires: C, 36.6; H, 3.7; N, 19.9%); ν_{max} (ATR)/ cm^{-1} 3151, 2964, 2053, 1651, 1593, 1526, 1414, 1392, 1256, 1166, 923, 749, 668, 480.

4.4. (BEDT-TTF)₄[Cr(NCS)₆].C₆H₅NO₂

To the anodic side of an H-shaped electrochemical cell fitted with a glass frit was placed BEDT-TTF (10 mg, 0.02 mmol), and to the cathodic side of the cell was added a solution of **2** (40 mg, 0.07 mmol) in nitrobenzene/acetonitrile (50:50 v/v, 25 mL). The level of solvent in each compartment was allowed to equilibrate, and to each side was inserted a platinum-tipped electrode. A constant current of 0.2 μ A was applied across the cell for 2 weeks, affording black blocks on the anode. These were harvested, washed with acetone and dried, m.p. 208 °C; Raman/cm⁻¹ ν_4 = 1430–1465 (broad); ν_3 = 1493–1497 cm⁻¹.

4.5. X-ray crystallography for (BEDT-TTF)₄[Cr(NCS)₆].C₆H₅NO₂

Synchrotron diffraction data were measured at the Daresbury SRS station 9.8. Crystal data for 4(C₁₀H₈S₈).Cr(NCS)₆.C₆H₅NO₂: M = 2062.17, black block, $0.20 \times 0.20 \times 0.10$ mm³, monoclinic, space group $P2_1$ (No. 4), a = 11.795(2), b = 20.144(4), c = 16.395(3) Å, β = 101.03(3)°, V = 3823.5(13) Å³, Z = 2, D_{calc} = 1.791 g/cm³, F_{000} = 2092, Bruker SMART APEX2 CCD diffractometer, synchrotron radiation, λ = 0.6942 Å, T = 120(2) K, $2\theta_{\text{max}}$ = 59.5°, 39216 reflections collected, 20865 unique (R_{int} = 0.0356). Final GOF = 1.119, R_1 = 0.0510, wR_2 = 0.150, R indices based on 19698 reflections with $F^2 > 2\sigma$ (refinement on F^2), 902 parameters, 2 restraints. Semi-empirical absorption corrections applied, μ = 1.142 mm⁻¹. Refined as racemic twin (54:46).

All crystal structures were solved with SHELXS-86 [43] and refined with SHELXL-97 [43], using the X-SEED interface [44]. Geometric analysis was made with PLATON [45], and illustrations were made with MERCURY [46].

4.6. (BEDT-TTF)₄[Cr(NCS)₆].CH₃CN

To the anodic side of an H-shaped electrochemical cell fitted with a glass frit was placed BEDT-TTF (10 mg, 0.02 mmol), and to the cathodic side of the cell was added a solution of **3** (40 mg, 0.07 mmol) in nitrobenzene/acetonitrile (50:50 v/v, 25 mL). The level of solvent in each compartment was allowed to equilibrate, and to each side was inserted a platinum-tipped electrode. A constant current of 1.0 μ A was applied across the cell for 1 week, affording black needles on the anode. These were harvested, washed with acetone and dried, m.p. 211 °C; Raman/cm⁻¹ ν_4 = 1416, ν_3 = 1460 cm⁻¹.

4.7. X-ray crystallography for (BEDT-TTF)₄[Cr(NCS)₆].CH₃CN

Crystal data for 4(C₁₀H₈S₈).Cr(NCS)₆.CH₃CN: M = 1980.12, black plate, $0.20 \times 0.04 \times 0.01$ mm³, triclinic, space group $P\bar{1}$ (No. 2), a = 10.291(2), b = 11.825(2), c = 16.738(3) Å, α = 86.55(3)°, β = 84.07(3)°, γ = 67.26(3)°, V = 1868.1(7) Å³, Z = 1, D_{calc} = 1.760 g/cm³, F_{000} = 1974, Bruker-Nonius APEX II CCD diffractometer with Bruker-Nonius FR591 rotating anode and 10 cm confocal mirrors, λ = 0.71073 Å, T = 120(2) K, $2\theta_{\text{max}}$ = 55.5°, 34511 reflections collected, 8565 unique (R_{int} = 0.074). Final GOF = 1.109, R_1 = 0.116, wR_2 = 0.198, R indices based on 5822 reflections with $F^2 > 2\sigma$ (refinement on F^2), 406 parameters, 12 restraints. Semi-empirical absorption corrections applied, μ = 1.126 mm⁻¹.

4.8. (BEDT-TTF)₇[Cr(NCS)₅(NH₃)₂].2.74C₂H₅OH.0.26H₂O

To the anodic side of an H-shaped electrochemical cell fitted with a glass frit was placed BEDT-TTF (10 mg, 0.02 mmol), and to the cathodic side of the cell was added a solution of **3** (40 mg, 0.07 mmol) in chlorobenzene/ethanol (60:40 v/v, 25 mL). The level

of solvent in each compartment was allowed to equilibrate, and to each side was inserted a platinum-tipped electrode. A constant current of 1.0 μ A was applied across the cell for 11 days, affording dark blocks on the anode.

4.9. X-ray crystallography for (BEDT-TTF)₇[Cr(NCS)₅(NH₃)₂].2.74C₂H₅OH.0.26H₂O

Crystal data for 7(C₁₀H₈S₈).2(Cr(NCS)₅(NH₃)).2.74(C₂H₅OH).0.26(H₂O): M = 3542.72, dark brown slab, $0.11 \times 0.08 \times 0.04$ mm³, triclinic, space group $P\bar{1}$ (No. 2), a = 12.5356(3), b = 14.7829(4), c = 19.3336(4) Å, α = 73.3040(10)°, β = 76.6790(10)°, γ = 86.8200(10)°, V = 3339.17(14) Å³, Z = 1, D_c = 1.762 g/cm³, F_{000} = 1804, Bruker-Nonius APEX II CCD diffractometer with Bruker-Nonius FR591 rotating anode and 10 cm confocal mirrors, σ = 0.71073 Å, T = 120(2) K, $2\theta_{\text{max}}$ = 55.5°, 98658 reflections collected, 15210 unique. Final GoF = 1.12, R_1 = 0.069, wR_2 = 0.14, R indices based on 12333 reflections with $F^2 > 2\sigma$ (refinement on F^2), 737 parameters, 6 restraints. Semi-empirical absorption corrections applied, μ = 1.247 mm⁻¹, refined as a non-merohedral twin (3:1).

4.10. X-ray crystallography for (BEDT-TTF)₇[Cr(NCS)₅(NH₃)₂].3CH₂Cl₂

The original data [32] were used for refinement of a model which included a disordered dichloromethane molecule at the centre of the “tube” motif. Crystal data: 7(C₁₀H₈S₈).2(Cr(NCS)₅(NH₃)).3(CH₂Cl₂), M_r = 3666.16, triclinic, space group $P\bar{1}$ (No. 2), a = 12.553(3), b = 14.766(3), c = 19.682(4) Å, α = 71.61(3), β = 76.67(3), γ = 87.28(3)°, V = 3367.4(13) Å³, Z = 1, D_c = 1.808 g/cm³, F_{000} = 1856, λ = 0.71073 Å, T = 293(2) K, R_1 = 0.043, wR_2 = 0.075, R indices based on 2544 reflections with $F^2 > 2\sigma$ (refinement on F^2).

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Appendix A.

CCDC 1062492–1062494 contains the supplementary crystallographic data for the three BEDT-TTF salts whose structures are reported. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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